Liquid crystalline dendrimer: Sythesis and Chracterization

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Abstract:

A new family of nematic liquid crystal dendrimers derived from 3,5-dihydroxybenzoic acid were synthesized. The synthesis of the dendrimers compounds shows the influence of the dendritic core on the mesomorphic properties. The liquid crystalline properties were studied by polarizing optical microscopy (POM) equipped with a hot stage, the structures of the synthesized compounds characterized using FTIR and ^{1}HNMR spectroscopy.

Key words: dendrimer, crystalline

Introduction:

In the late 70´s Vögtle and Tomalia developed independently the first synthesis of a new kind of compounds which they called dendrimers (from the Greek *dendri*: tree branch and *mer:* part). Dendrimeric materials have recently become of great interest in supramolecular chemistry, mainly due to the possibility of obtaining well defined macromolecules [1].

Dendrimers are highly branched three dimensional macromolecules with a branch point at each monomer unit and have attracted interest of both industrial and academic chemists. The most important feature of dendritic molecules is their well defined shape, symmetric nature and molecular architecture, which is not observed in case of hyper branched polymers [2].

Also unlike hyper branched polymers, dendrimers are obtained by careful stepwise growth of successive layers of generations. It is possible to functionalise dendrimers at the periphery of the globular structure instead of insulating a reactive site at the centre of a dendrimer. Besides amphiphilic dendrimers containing an extended rigid block represents a class of self assembling systems those are increasingly used for the construction of supramolecular architecture with well defined shape.

Nowadays a broad range of dendrimers are available and some of them are even available commercially, and have found to be promising towards important chemical processes and also as drug or gene delivery devices, as carriers for catalytically active site in flow reactors and also as chiral auxiliaries for asymmetric synthesis [3]. The field of research on the look for newer dendritic species has also been boosted up by the enhanced possibility of their potential in wide spread application [4]. Their resemblance and similar dimensions to some living components and to molecular functional materials projects them as potential candidate for even biological science too, provided these are suitably functionalised. High molecular weight monodisperse dendrimers are promising candidates for the development of new liquid-crystalline materials for specialized application [5].

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Instruments and Equipments

Fourier Transform Infrared Spectrometer (FT.IR)

FTIR spectra in the range (4000-400) cm^{-1} were recorded using potassium bromide disc on FT.IR instrument Model 8300 Shimadzu Spectrophotometer, Japan.

Melting Points

Uncorrected melting points were recorded on hot stage ***Gallen kamp*** melting point apparatus (U.K.)

Hot-stage Polarizing Microscope

The optical behavior observations were made using MEIJI microscope equipped with INSTEC hot stage and central processor controller mK 1000 and connected with Lumenera color video camera. This analysis was carried out in the chemistry department of AL- Nahrain University.

Preparation of 4- hydroxy -4`- nitro phenyl imine (1)

A mixture of p-hydroxy benzaldehyde (1.22 g , 0.01 mole) in absolute ethanol (15 ml) with two drops glacial acetic acid, stirring in room temperature then add to p-nitroaniline (1.38 g ,0.01 mol). Refluxed the mixture with stirring for four hours at the range temperature (60 -70° C). The formed precipitation was filtrated and dried to give 4- hydroxy -4`- nitro phenyl imine (1) which have yellow color and physical properties are listed in table 1.

Synthesis of 4-(2-chloroethoxy)phenyl-4`-nitrophenylimine (2)

Add (5g, 0.037) of K_2CO_3 dissolved in (6 ml) of dichloroethane then stirring in room temperature and add (1.75 g, 0.0072 mole) of compound (1) then refluxed with stirring for four hours. The formed precipitation was filtrated and dried to give 4-(2- chloroethoxy) phenyl-4`-nitrophenylimine (2), physical properties are listed in table 1.

Preparation of 3,5-dihydroxy methyl benzoate [6] (3)

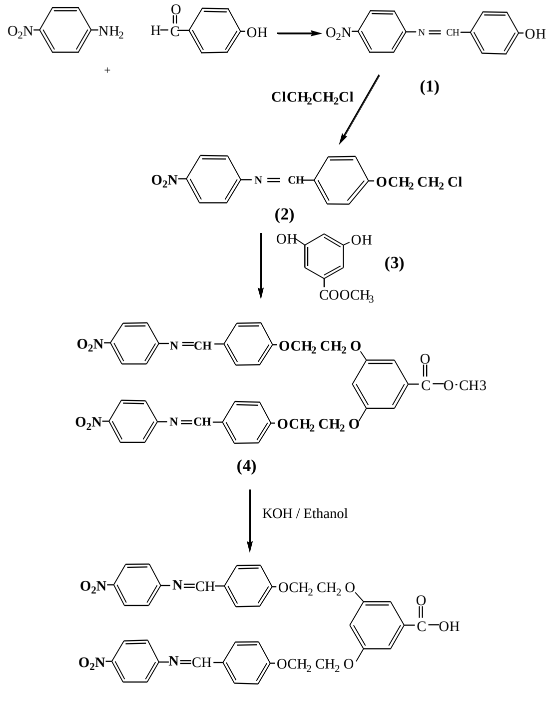
Dissolve (1.23 g, 0.008 mole) of 3,5-dihydroxy benzoic acid which have white color in (2 ml) of absolute methanol and one drop of H_2SO_4 then refluxed with stirring for four hours to give 3,5-dihydroxy methyl benzoate which have white color and physical properties are listed in table 1.

Synthesis of 3,5-di-[4``-nitrophenyl-4`-ethylene-1,2-dioxy) phenylimine] methyl bezoate (4)

(0.047g, 0.0028 mole) of 3,5-dihydroxy methyl benzoate was added to compound (2) (1.75g, 0.0057 mole) in 10 ml acetone. The mixture was refluxed with stirring for four hours and filtered to give precipitation of G_1 which have physical properties are listed in table 1.

Synthesis of 3,5-di-[4``-nitrophenyl-4`-ethylene-1,2-dioxy)phenylimine] benzoic acid G_1

Prepare (2.5 g, 0.04 mole) of KOH in (25 ml) of ethanol, then take (25 ml) of this solution and add (4.01g, 0.0057 mole) of (4) then refluxed with stirring for two hours and add ice water with HCl and filtered to give precipitation of G_1, melting point is listed in table 1.



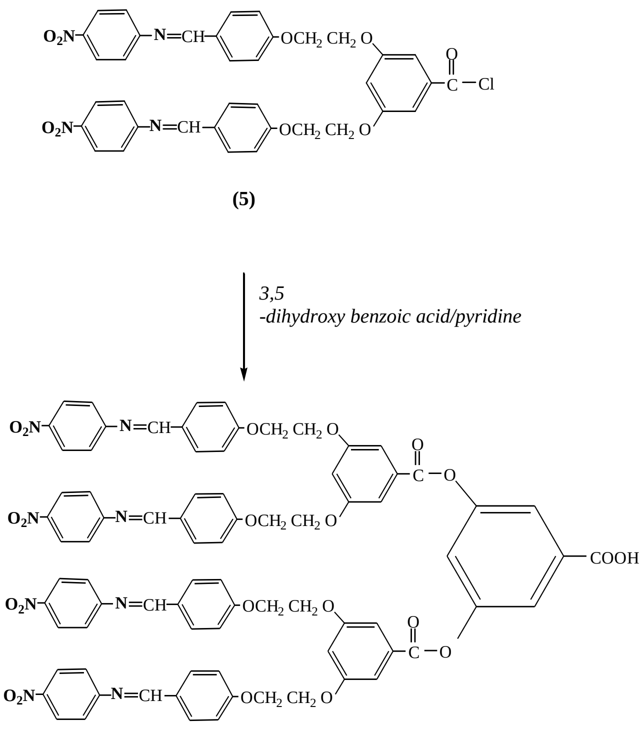
G_1

Synthesis of 3,5-di-[4``-nitrophenyl-4`-ethylene-1,2-dioxy) phenylimine] benzoylchloride (5)

Mixtures of (1g, 0.001 mole)) G1 in (5 ml) of thionyl chloride ($SOCl_2$) with two drops of DMF then refluxed with stirring for five hours then remove the reflux condenser to evaporate the excess of ($SOCl_2$) and filtered to give precipitation of (5).

Synthesis of 3,5-Bis-[3`,5`-di-(4```-nitrophenyl-4``ethylene-1,2-dioxy) phenylimine] benzoic acid G_2

Dissolve (1 g, 0.006 mole) of 3,5-dihydroxy benzoic acid in (5 ml) of pyridine, then add compound (5) to the above mixture drop by drop with stirring for four hours in ice bath. Poured the mixture onto an ice water with two drops of conc. HCl to get precipitation then filtered and dried to give precipitation of G_2, have physical properties are listed in table 1.



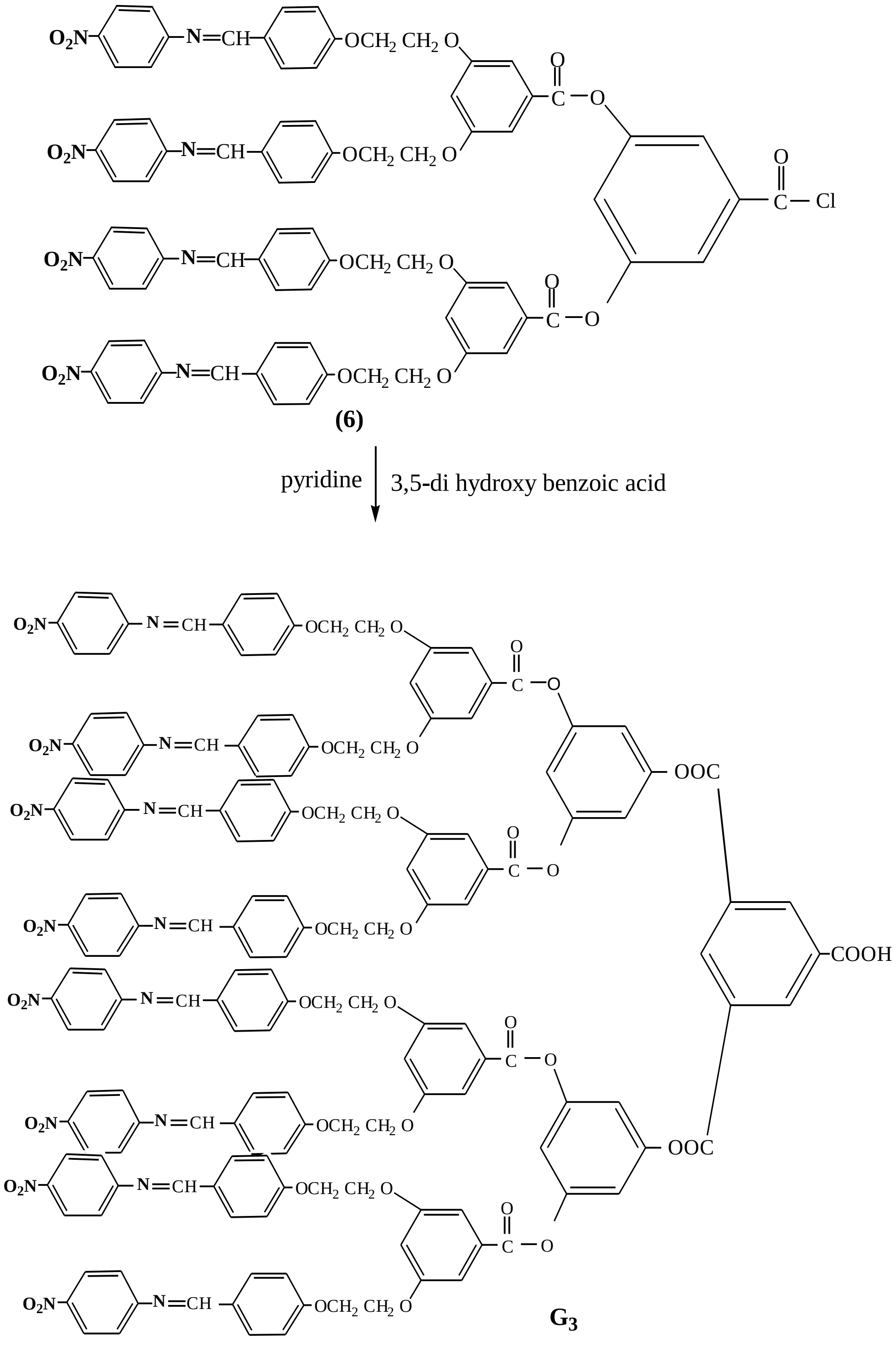
G_2

Synthesis of 3,5-Bis-[3`,5`-di-(4```-nitrophenyl-4``ethylene-1,2-dioxy) phenylimine] benzoylchloride (6)

Dissolve (1 g, 0.00075 mole) G_2-COOH in (5 ml) of thionyl chloride ($SOCl_2$) with two drops N,N-dimethyl formamide (DMF) Refluxed the mixture with stirring for five hours then remove the reflux condencer to evaporate the excess of ($SOCl_2$) and filtered and dried to give precipitation of compound (6), physical properties are listed in table 1.

Synthesis of 3,5-Bis-[3`,5`-bis-{3``,5``-di-(4```-nitrophenyl-4``ethylene-1,2-dioxy) phenylimine}] benzoicacid G_3

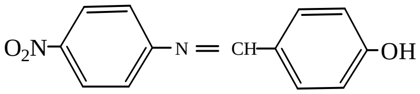
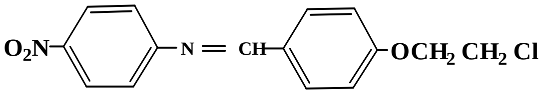
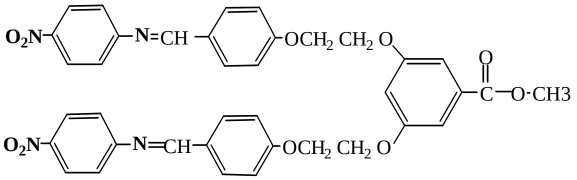
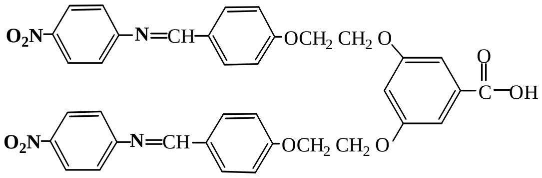
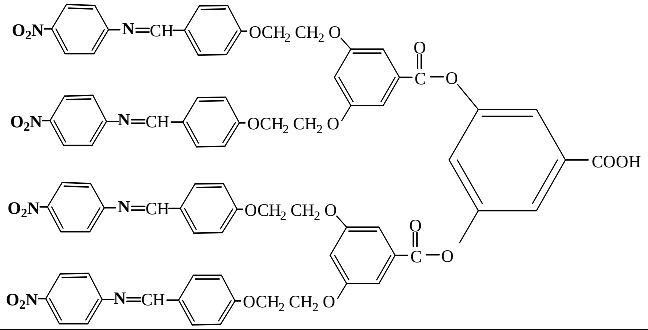
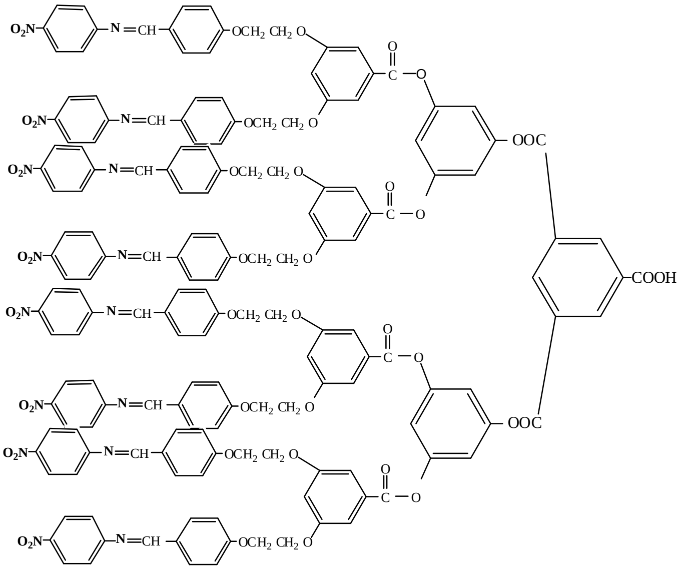
Dissolve (1 g, 0.006 mole) of 3,5-dihydroxy benzoic acid in (5 ml) of pyridine, then add compound (6) to the above mixture drop by drop with stirring for four hours in an ice bath then poured onto an ice water with two drops of HCl to get precipitation then filtered to give precipitation of G_3, physical properties are listed in table 1.


O$_2$N
N=CH
OCH$_2$ CH$_2$ O
C—O
C—Cl
pyridine
3,5-di hydroxy benzoic acid
OOC
COOH

(6)

G$_3$

Table 1 Melting point and %yield of prepared compounds

Comp. No.	structure	Melting point	% Yield
1		**128-138° C**	**68%**
2		**142-148 ° C**	**75%**
4		**167-169° C**	**69%**
G_1		**225-270° C**	**72%**
G_2		**261-278° C**	**76%**
G_3		**272-288° C**	**70%**

Result and Discussion

Figure 1 shows the FTIR spectrum of compound (1) using KBr disc (cm^{-1}) which showed the disappearance of NH_2 bands of the amine and the appearance of bands at 3249.4, 1630.4, 1557.8 and 1350.0 cm^{-1} for O– H, HC=N stretching for the imine group and NO_2 stretching.

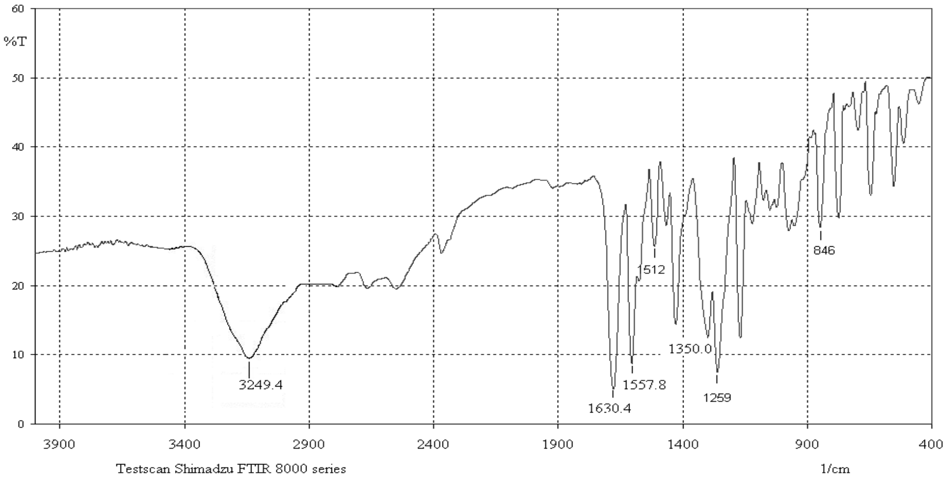


Fig.1 FTIR spectrum of 4- hydroxy -4`- nitro phenyl imine (1).

Reaction between 4- hydroxy -4`- nitro phenyl imine with dichloroethane yield compound (2). The product was verified by FTIR spectral data. The spectrum is shown in Figure 2. The appearance of bands at 2951.1 cm^{-1}and 2891.1 cm^{-1} that are due to C – H aliphatic stretching. A new stretching band appeared at 1172.6 cm^{-1} which could be attributed to C – O stretching of ether group and a band at 650.6 cm^{-1} due to C – Cl bond.

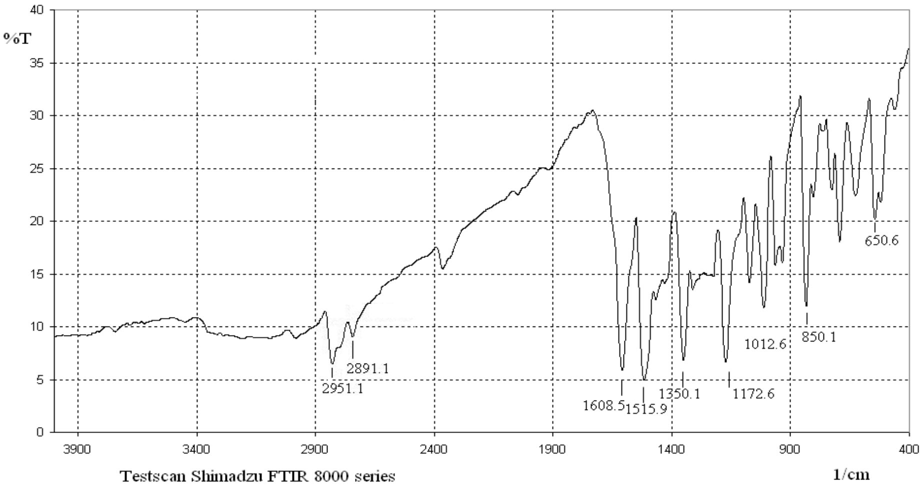


Fig. 2: FTIR spectrum of 4-(2- chloroethoxy)phenyl-4`-nitrophenylimine (2)

To prepare compound (4) firstly, we prepared 3,5-dihydroxymethyl benzoate (3) from esterfication of 3,5-dihydroxhbenzoic acid with methanol in basic media. Secondly, we synthesized compound (4) through the reaction of compound (2) with the prepared ester (3), according to nucleophilic substitution mechanism. The structure of this compound was elucidated by FTIR spectroscopy. The FTIR spectrum of this compound is shown in Figure 3. The spectrum shows bands at 2929.2 and 2897.6 which assign to C –H aliphatic stretching. The spectrum also revealed a carbonyl absorption band of ester group at 1739.2 cm^{-1} and an absorption C – O – C stretching band at 1259.5 cm^{-1}.

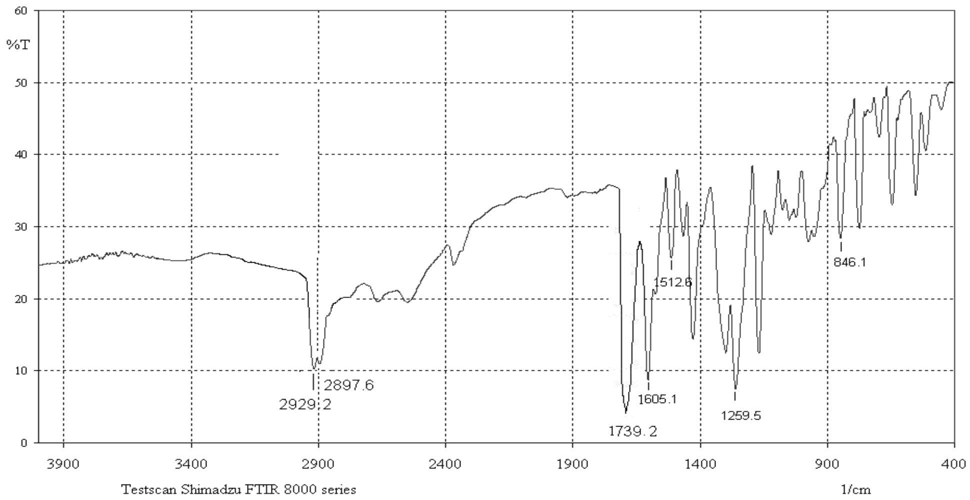


Fig. 3 FTIR spectrum of 3,5-di-[4``-nitrophenyl-4`-ethylene-1,2-dioxy) phenylimine] methyl bezoate (4)

The hydrolysis of compound (4) under basic condition will give compound G1 which represent the first generation of the dendrimer compound. The product was characterized by FTIR and ^{1}HNMR spectroscopy. The FTIR spectrum of G_1 is shown in Figure 4 which showed the appearance of the absorption bands at 3345.4 due to O–H stretching of carboxyl group and bands at 1720.5, 1630, 1557.8, 1350.0 and 846.4 which attributed to acid carbonyl, imine group, nitro group and out of plane bending of para-disubstituted benzene ring.

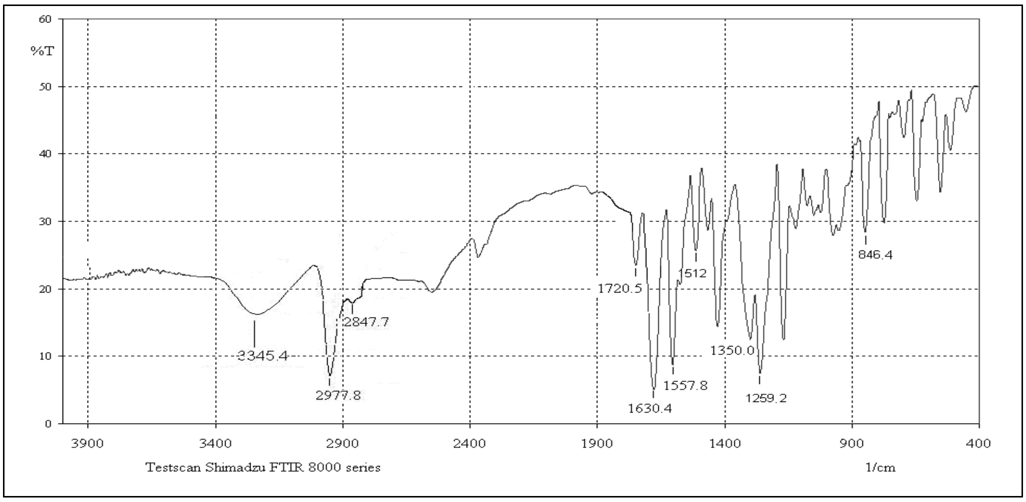


Fig. 4 FTIR spectrum of 3,5-di-[4``-nitrophenyl-4`-ethylene-1,2-dioxy) phenylimine] benzoic acid G_1

The ^{1}HNMR spectrum of G1 is shown in Figure 5. The following characteristic chemical shifts (DMSO, ppm) were appeared: a doublet of doublets leaning on each other at δ 7.9 – 8.1 that could be attributed to the aromatic protons. The spectrum also showed a singlet at δ 11.217 that could be assigned to the carboxylic acid proton. An eight proton triplet at δ 4.1 ppm could be assigned to the –OCH_2CH_2O group. The ^{1}HNMR spectrum is in agreement with the proposed structure.

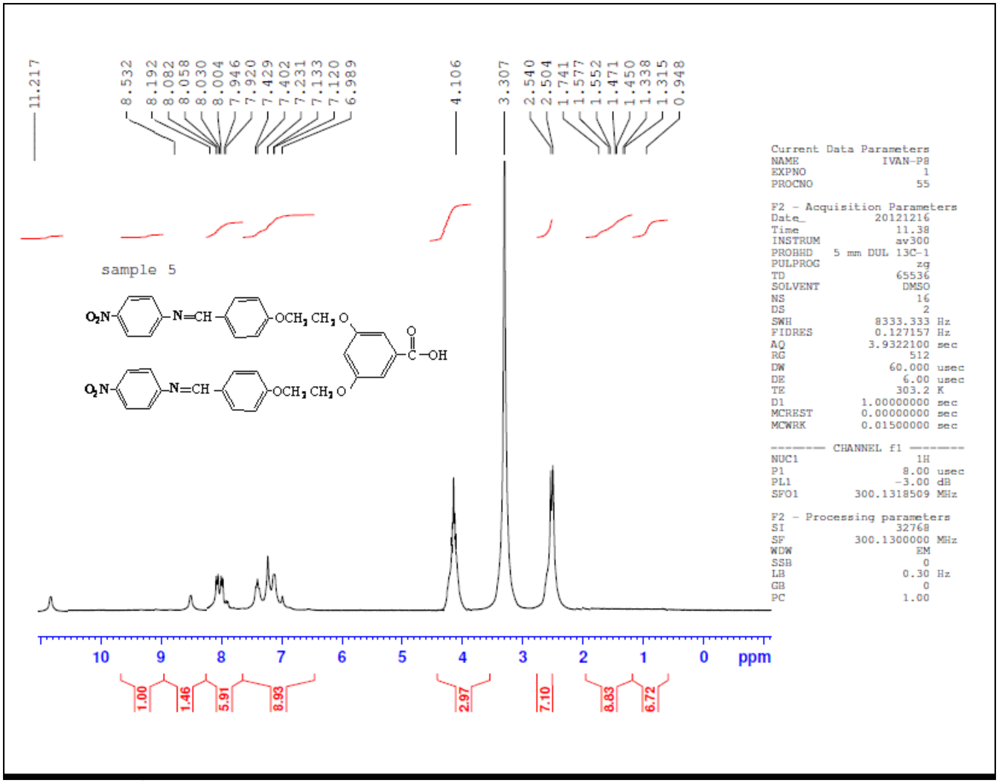


Fig. 5: ^{1}HNMR spectrum of 3,5-di-[4``-nitrophenyl-4`-ethylene-1,2-dioxy)phenylimine] benzoic acid G_1

The second generation of the dendrimer was synthesized through two step, the first step involve the internal nucleophilic substitution (S_Ni) reaction between G_1 with thionyl chloride The second step represented by the reaction of the synthesized acid chloride with 3,5-dihydroxy benzoic acid by nucleophilic substitution (tetrahedral mechanism) by the two step: firstly, the addition of nucleophile (O – H) to the carbon of the carbonyl group, secondly the elimination of the leaving group (Cl).

The synthesized compound (G_2) was characterized by FTIR (KBr, cm^{-1}) are shown in Figure 5. It showed the appearance of bands at 3254.1 that due to O–H stretching of carboxylic acid. A bands appeared at 2924.9 and 2887.3 which assign to C – H aliphatic stretching. The spectrum also shows bands at 1735.0, 1702.4, 1587.6, 1247.8 and 840.9 which could be attributed to C = O stretching of ester, acid, CH=N stretching of imine group, C – O – C of ester group and out of plane bending of γ-disubstituted benzene ring.

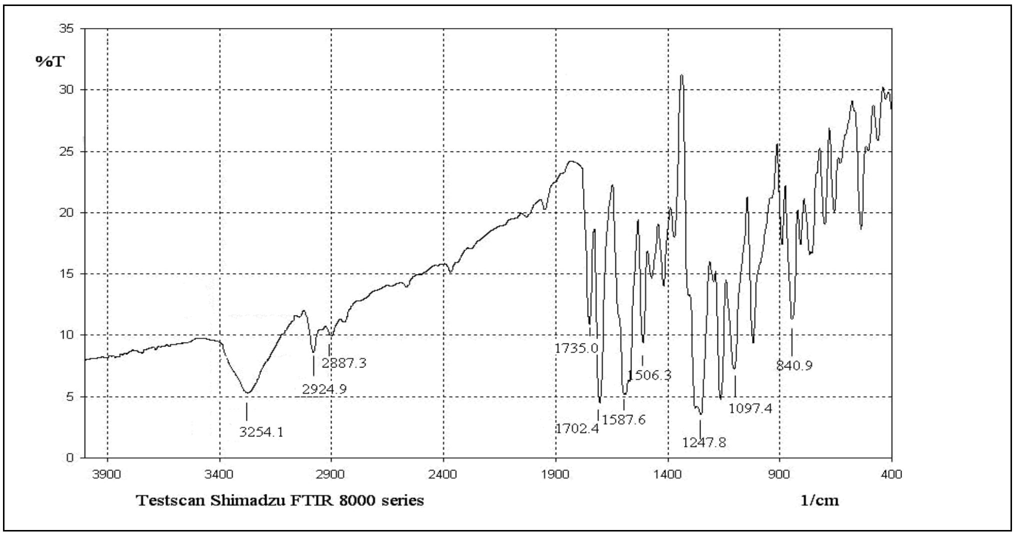


Fig. 6: FTIR spectrum of 3,5-Bis-[3`,5`-di-(4```-nitrophenyl-4``ethylene-1,2-dioxy) phenylimine] benzoic acid G_2

The third generation of the dendrimer was synthesized by the same steps that used for G_2. The synthesized compound (G_3) was characterized by FTIR (KBr, cm^{-1}) are shown in Figure 6. It showed the appearance of bands at 3326.9 that due to O–H stretching of carboxylic acid. The spectrum also shows bands at 1730.8, 1680.8, 1595.5, 1220.7 and 844.7 which could be attributed to C = O stretching of ester, acid, CH=N stretching of imine group, C – O – C of ester group and out of plane bending of γ-disubstituted benzene ring.

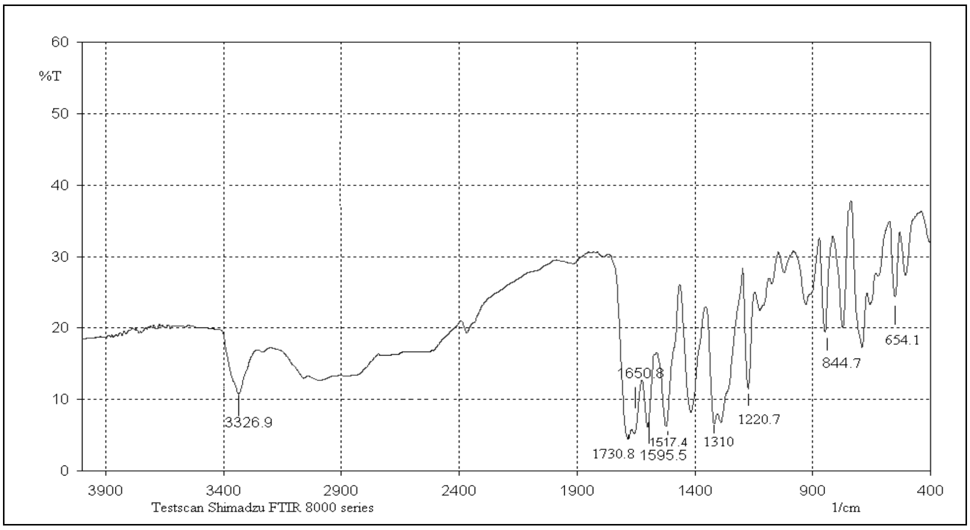


Fig. 7: FTIR spectrum of 3,5-Bis-[3`,5`-bis-{3``,5``-di-(4```-nitrophenyl-4``ethylene-1,2-dioxy)phenylimine}]benzoicacid G_3

Liquid Crystalline Properties of the Synthesized Compounds G_1, G_2,G_3:

The combination of mesomorphic properties and dendritic structures is a new approach in the field of liquid crystals. The interest in the construction of such multifunctional, practically monodisperse, macromolecular objects arises from their ability to self-assemble into mesophases and from their potential utilization as photonic, electronic, and ionic transport based-applications, depending on the functionality sought.1 Moreover, owing to their branched nature, liquid crystal dendrimers possess properties halfway between those of polymers and of single monomeric species [7].

The incorporation of mesogenic units at the periphery of dendrimers gives rise to an interesting phenomenon, namely, the struggle between the preferred arrangements of the dendrimer core and the peripheral mesogenic units [8]. To minimize their free energy, dendrimers tend to adopt a 3D spherical structure, but the attachment of anisotropic mesogenic units causes this globular shape to be distorted because of the strong interactions between such units. Indeed, liquid crystalline phases can arise in this type of system. McKenna et al. [8] showed that the attachment of rodlike units gives both nematic and smectic phases17-19 which occur because of the parallel alignment of the mesogenic units with respect to one another. Such an arrangement causes the dendrimer core to be distorted from its ideal conformation.

The mesomorphic properties of the materials were investigated by polarizing optical microscopy (POM). Compounds **G_1, G_2, G_3** showed a nematic mesophase of a typical thread-like texture as shown in Figures (3.7 – 3.9). The phase transition temperatures of the materials are given in table 2.

Table 2 Phase transition temperatures of synthesized demdrimer

No.	Type of transition	Temp. of transition °C
G_1	C ⟶ N	221-226
G_2	C ⟶ N	236-243
G_3	C ⟶ N	251-260

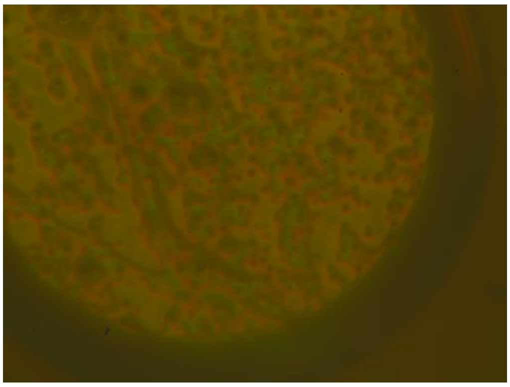


Fig. 8: Nematic texture of G_1

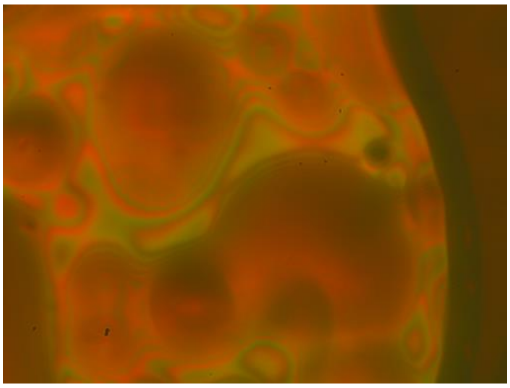


Fig.9: Nematic texture of G_2

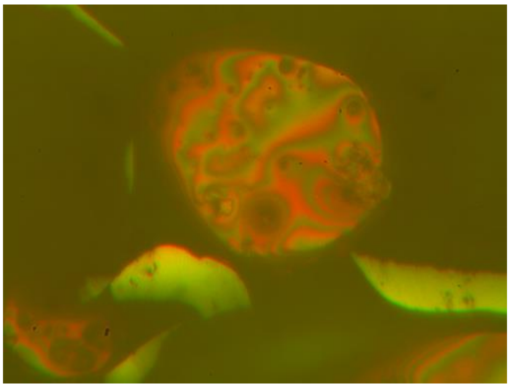


Fig. 10: Nematic texture of G_3

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بلورات سائلة شجيرية : تحضير و تصنيف

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الخلاصة:

تم تحضير عائلة جديدة من المركبات البلورية السائلة الشجيرية مشتقة من 4،5-ثنائي هيدروكسي حامض البنزوك. تم ملاحظة تأثير محور التفرع على الخواص البلورية السائلة. تمت دراسة الخواص البلورية السائلة للمركبات المحضرة باستخدام مجهر الضوء المستقطب المزود بمسخن، كذلك تم تسخيص تراكيب المركبات باستخدام مطيافية الاشعة تحت الحمراء (FTIR) ومطيافية الرنين النووي المغناطيسي للبروتون (^{1}HNMR).